Mass Spectrometric Investigations of the Atmosphere between 100 and 227 Kilometers above Wallops Island, Virginia

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Abstract. The diffusive separation of argon and nitrogen was measured by means of a Bennett radio frequency mass spectrometer carried on an Aerobee 150A rocket (NASA 4.14) launched at 1141 EST, November 15, 1960. The primary purpose of the spectrometer measurements was to obtain temperate latitude diffusive separation data to compare with those measurements obtained in the arctic (Fort Churchill, Canada) during the International Geophysical Year. The results indicate that diffusive separation occurred above about 110 km and that the altitude profile of the A/N₂ ratio is similar to that obtained during the two night flights in the arctic atmosphere.

Introduction

As one of the initial efforts in the NASA program for studying the structure of planetary atmospheres, the Aerobee 150A rocket NASA 4.14 was instrumented with Bennett radio frequency mass spectrometers patterned after those used by the Naval Research Laboratory for the IGY [*Meadows and Townsend*, 1960; *Johnson*, 1961]. The principal purpose was to measure the effectiveness of diffusive separation in the atmosphere as indicated by the distribution of argon and molecular nitrogen between 100 and 150 km. This payload, flown from Wallops Island, Virginia, on November 15, 1960, provided the first successful U. S. measurement of this type at a location other than Fort Churchill, Canada. A somewhat similar series of flights was made in the middle latitudes of the USSR by Soviet scientists in 1959, 1960, and 1961 [*Pokhunkov*, 1960, 1962, 1963a, b; *Istomin and Pokhunkov*, 1963].

Instrumentation

The rocket NASA 4.14 was instrumented by the Goddard Space Flight Center to obtain, from 100 km to the peak of flight, information about the neutral particles and positive ions in the earth's atmosphere. The instruments used were Bennett radio frequency mass spectrometers and a Bayard-Alpert ionization pressure gage. The locations of the various sensors are shown in Figure 1.

The mass spectrometer for measuring the neutral particle composition of the atmosphere differed from those used during the IGY in that a 7-5 cycle three-stage analyzer was used, with a resolution of about 1 part in 25. This configuration was selected instead of the four-stage IGY version to obtain greater sensitivity as well as linear operation at higher pressures. The entrance geometry and ion source, however, remained unchanged and were as pictured in earlier reports [*Meadows and Townsend*, 1958, 1960]. The electronic circuitry was also substantially the same as that used during the IGY, and included an emission regulator for the filament; an RF oscillator, from which the bias and stopping potentials for the analyzer were derived; a motor-driven potentiometer for the voltage sweep; a 100% negative feedback dc amplifier to measure the ion current; and suitable regulated power supplies. The mass range of 8 to 48 amu was swept once each 1.4 seconds. The ion source used 45-volt electrons at a nominal current of 10 ma. Other operating potentials were: RF potential, 7.17 vrms at 4.2 Mc/s; bias, 15.4 volts; and stopping, 44.8 volts.

Laboratory calibrations of the mass spectrometer included the admission of dry air through a molecular-flow type variable leak. Four calibration runs on different days with various settings of operating potentials were plotted as Ar$^+$/N$_2^+$ versus pressure over the pressure range from 10^{-6} to almost 10^{-3} mm Hg: the points had a scatter of ±15% about the curve drawn in Figure 2. Also plotted in Figure 2 is the ratio of the argon and molecular nitrogen currents as
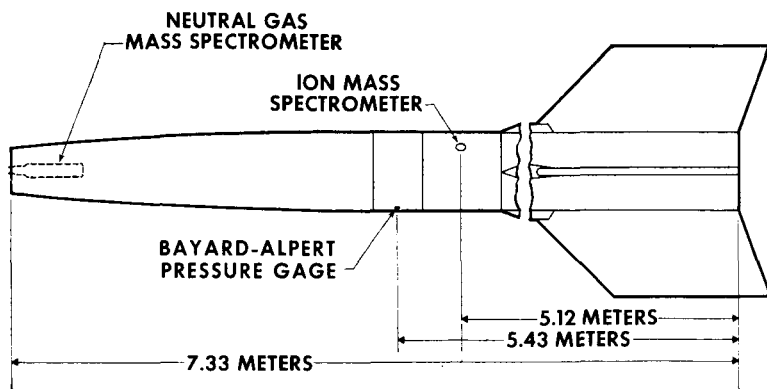
Fig. 1. The locations of the three principal sensors on NASA 4.14. These positions were chosen to obtain maximum isolation of the experiments from each other. The sun and earth sensors for aspect determination are on the hidden side.

a function of the total pressure in the mass spectrometer. This ratio was found to be independent of stopping potential and of electron emission over the range of these potentials expected in flight. The ratio was independent of pressure below about 5×10^{-5} mm Hg, but increased slowly at higher pressures as a consequence of the relatively greater probability for collisions of N_2^+ with the neutral particles. The total ion current, which is the sum of the individual ion currents at the various mass numbers, was used as a monitor of the total pressure within the tube. The pressure calibration was obtained by means of a VG-1A ionization pressure gage adjacent to the mass spectrometer on the vacuum system. Total spectrometer ion current was linear with respect to pressure up to 4×10^{-5} mm Hg and had its maximum value at 4.3×10^{-4} mm Hg.

After calibration of the spectrometer was completed, the tube was evacuated, baked, and sealed. A getter, confined to the removable tip, was flashed. The tube was then sealed with O-ring gaskets to a bulkhead at the forward end of the rocket, about 19 inches back from the nose tip. After the top 19 inches of the rocket and the tip of the spectrometer were removed during flight at an altitude of 100 km, the tubulation of the spectrometer extended slightly above the bulkhead. The opening did not 'see' any part of the surface of the vehicle.

DATA

The experiment was flown from Wallops Island, Virginia (latitude 37°50′06″N, longitude 75°29′11″W), at 1141 EST, November 15, 1960, to an altitude of 227.3 km. The basic information about the flight of the rocket is given in Table 1. The angle of attack is the angle between the total velocity vector of the rocket and the longitudinal axis of the spectrometer. Up to 172.4 seconds the positions and velocities were obtained from tracking radars; subsequent positions and velocities were computed for free-fall conditions. The peak altitude is known with an error of ±0.5 km. The direction of the rocket axis was determined from two rocket-mounted magnetometers and a sun-earth sensor with an accuracy of ±3 deg. After thrust termination, the rocket's horizontal velocity was constant at 0.145 km/sec in a direction 152 deg east of north, until the vehicle re-entered at about 85 km. The vehicle spun about its longitudinal axis at a rate of 2.69 rps and precessed in a cone of 4.6 deg half angle; the cone axis was tipped 10.8 deg from zenith in a direction 15.5 deg west of north.

The basic data obtained from the spectrometer are given in Figures 3, 4, 5, and 6. The output from the electrometer was telemetered on three channels, each of which covered about 1 order of magnitude. At low altitudes the efficiency of the mass spectrometer is reduced owing to the relatively high pressure in the mass spectrometer; the initial low currents in Figures 2, 3, and 4 are due to loss of ions by collision as they pass through the analyzer. The currents continue to decrease during the descent part of the flight because the vehicle descended nose upward. At 400 seconds, more than half, but
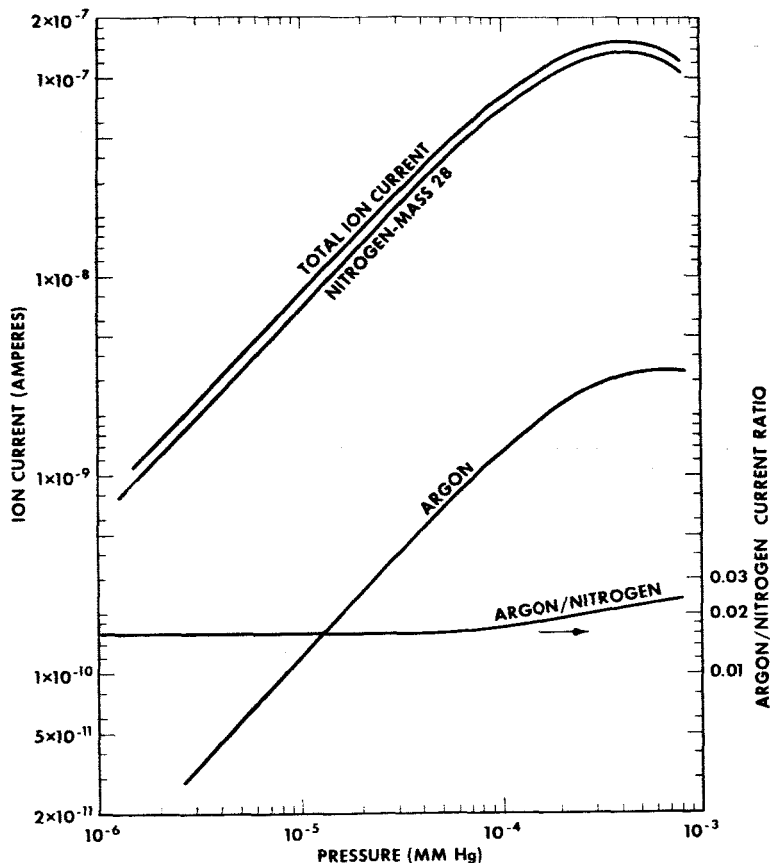
Fig. 2. Calibration data for the mass spectrometer flown in NASA 4.14. The curves have been adjusted so that the sensitivity corresponds to the operating conditions used in flight.

not quite all, of the total ion current observed is residual gas from the rocket vehicle. Finally, as the vehicle tips over, the pressure increases rapidly in the mass spectrometer and rises above its permissible operating region.

Figure 3 shows the spectrometer collector current due to nitrogen at 28 and 14 amu, argon at 40 amu, and the total ion current for these and the remaining species sensed by the spectrometer. The total does not include the current due to atmospheric ions. In Figure 3 the actual data points for molecular nitrogen and for argon are shown to indicate the scatter present in the various current and altitude ranges; the scatter is similar for the other constituents.

In Figure 4 are plotted the ion currents for oxygen at 34, 32, and 16 amu, nitric oxide at 30 amu, and a very small peak at 26 amu. In Fig-

ure 5 are plotted carbon dioxide appearing as currents at 44 and 12 amu, and water vapor at 18 and 17 amu.

The ambient atmospheric ions also enter the analyzer. Because the rocket acquires a negative potential of a few volts with respect to the ionosphere, the ions and their harmonics appear and both are displaced on the mass scale. Thus, the atomic oxygen ion appears at 15.3 amu, the molecular oxygen ion at 31.2 amu, and the nitric oxide ion at 29.4 amu. The lower harmonics appear in the spectrums at the following positions: 32^+ at 23.2 amu, 30^+ at 21.7 amu, 28^+ at 20.2 amu, and 16^+ at 11.4 amu. The fundamental peak for ambient 28^+ is obscured by the very large peak due to neutral nitrogen. The variations of these peaks with time and altitude are shown in Figure 6.

TABLE 1

Altitude	Total Velocity	ASCENT		DESCENT	
		Time	Angle of Attack	Time	Angle of Attack
Km Above Sea Level	Km/Sec	Sec	Degrees	Sec	Degrees
100	1.545	87.5	6.3	420.4	160.8
110	1.484	94.0	9.6	414.0	159.9
120	1.418	101.0	11.7	407.0	160.9
130	1.350	108.2	12.1	399.7	163.8
140	1.280	115.8	10.7	392.0	166.9
150	1.202	124.4	7.0	384.2	168.0
160	1.123	132.8	3.1	375.2	164.9
170	1.036	142.0	5.3	365.7	159.9
180	.942	152.5	10.3	355.7	157.2
190	.838	163.5	12.3	344.2	159.0
200	.722	176.8	8.8	331.3	163.1
210	.580	192.5	6.5	315.6	158.2
220	.393	214.1	20.5	294.1	145.3
225	.251	231.6	26.4	276.4	139.3
227.3	.145	253.75	82.0	253.75	82.0

ANALYSIS OF DATA

The effect of diffusive separation of the constituents of the atmosphere is noted by considering the data for argon and molecular nitrogen. A separation ratio r is defined in terms of atmospheric parameters and related mass spectrometer ion currents as

$$r = \frac{(\rho_{Ar}/\rho_{N_2})_{alt}}{(\rho_{Ar}/\rho_{N_2})_{ground}} = \frac{(28/40)^{1/2}(I_{Ar}/I_{N_2})_{alt}}{(I_{Ar}/I_{N_2})_{ground}}$$

where the current ratios for flight data and ground data are taken at the same total pressure in the mass spectrometer. (The total pressure in the mass spectrometer during flight was measured by the total ion current observed and the calibration curve of Figure 2.) In the above formula ρ_{Ar}/ρ_{N_2} represents the ratio of the density of argon and molecular nitrogen in the atmosphere. The subscript 'alt' refers to the measurement at a particular altitude, the subscript 'ground' refers to ground level air as used in laboratory calibration. I_{Ar}/I_{N_2} represents the ratio of the ion currents collected due to the argon and molecular nitrogen during flight or calibration, as indicated by the subscript. The current ratios are multiplied by the square root of the ratio of the mass of nitrogen to that of argon to take into account the difference in flow rate into and out of the mass spectrometer when its velocity with respect to the atmosphere is appreciably greater than thermal velocities [Meadows and Townsend, 1958].

The data used to calculate the separation ratio are given in Figures 2 and 3. During the period of interest, from 96 to 155 seconds, the emission current from the filament in the ion source ranged from 10.0 to 10.8 ma; however, all the plotted data have been normalized to a current of 10.0 ma. During the first few seconds of operation of the spectrometer tube in flight, that is, from 89 to 95 seconds, a glow discharge apparently occurred in the ion source, with the result that the values of ion currents were not proportional to emission current, and resolution of the spectrometer was impaired during that interval of time. The data from these spectrums were not used in the computations.

The result, the separation ratio, is shown in Figure 7. The points are derived from the values of the smooth curves in Figure 3, read at the altitudes in question. The error in this curve (Figure 7) is judged to be no more than ±20% from systematic and reading errors. The reading errors rise rapidly with altitude above 150 km; the extension of the separation ratio is shown in Figure 8 only to indicate the trend.

DISCUSSION

Ambient ions. Atmospheric ions also enter the spectrometer and appear in the spectrums, displaced about one-half a mass unit from ions of the same mass produced in the ion source. The data for these ions are shown in Figure 6. The relative altitude distribution of the ambient ions measured by the neutral gas spectrometer support the measurement of ion composition by the ion spectrometer on this vehicle as reported earlier by Taylor and Brinton [1961].

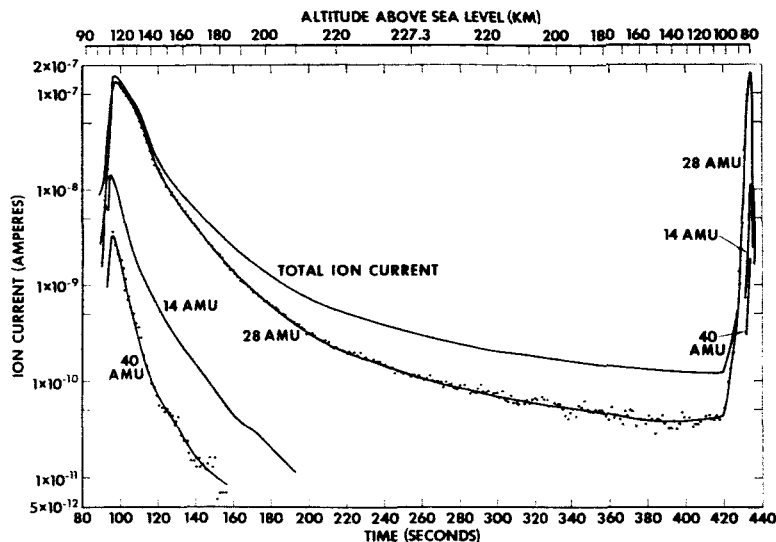Other gases. Little useful information about

Fig. 3. The major atmospheric gases, molecular nitrogen at 28 amu and argon at 40 amu, and the total ion current, which is a measure of the total pressure within the mass spectrometer.
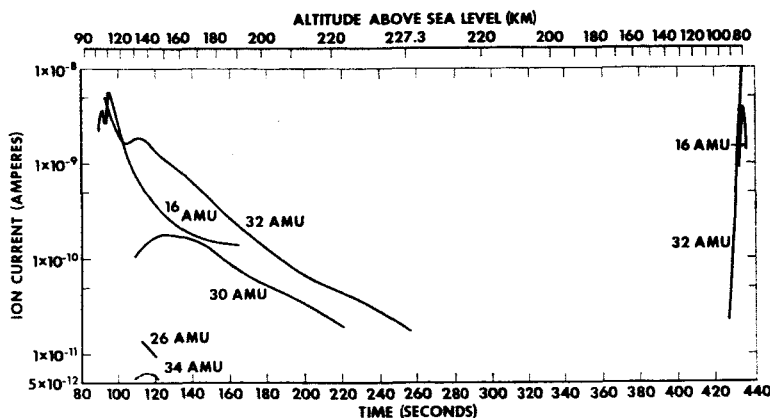

Fig. 4. Molecular and atomic oxygen, an unidentified peak at 26 amu, and the nitric oxide ion produced within the mass spectrometer by an ion-molecule reaction.

the upper atmosphere was obtained from the remaining ion current peaks. Mass number 14 (N^+) appears (Figure 3) as the result of dissociative ionization of molecular nitrogen within the spectrometer's ion source as well as from ionization of atomic nitrogen. All the mass 14 ion current in these spectrums is attributed to molecular nitrogen. Either any atmospheric atomic nitrogen disappeared on the surfaces of the spectrometer or its abundance is less than 4% of that of molecular nitrogen.

No completely plausible explanation has been found for the shape of the altitude profiles of

mass numbers 16 (O^+) and 32 (O_2^+) in Figure 4. It may be that immediately after the spectrometer was opened to the atmosphere both atomic and molecular oxygen were absorbed on the surfaces of the spectrometer. After 120 seconds, the principal source of molecular oxygen within the spectrometer might have been the gas released from these surfaces, the supply to the surface being constantly replenished by the oxygen atoms and molecules from the atmosphere. It does not seem possible to deduce from these data the relative abundance of atomic and molecular oxygen either with respect to
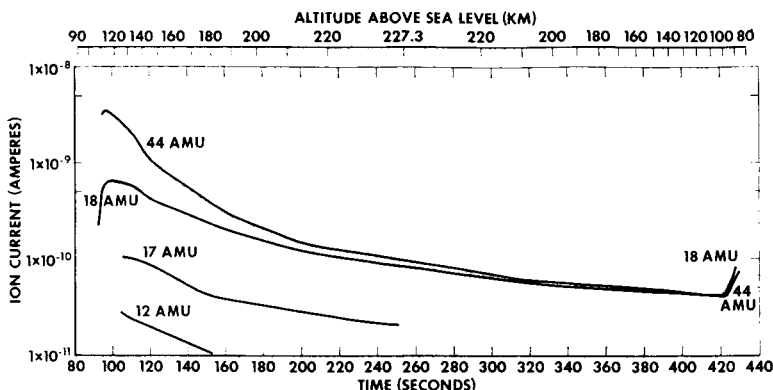
ALTITUDE ABOVE SEA LEVEL (KM)

Fig. 5.   Rocket gases: carbon dioxide and water vapor.
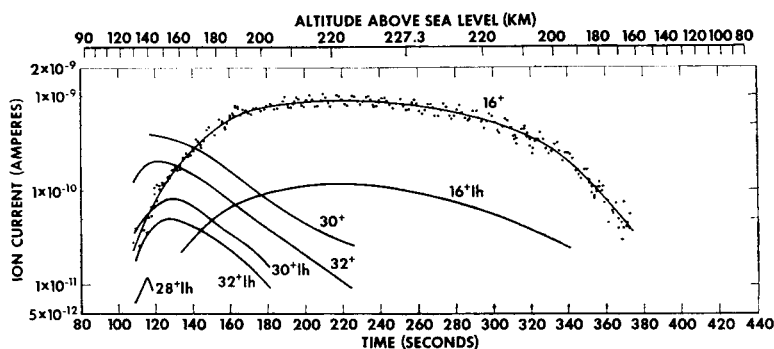
ALTITUDE ABOVE SEA LEVEL (KM)

Fig. 6.   Ambient ions and their harmonics. The fundamental peak of the 28⁺ ion was hidden
by the ions formed from the neutral nitrogen.

each other or with respect to the total atmosphere. Measurements with a mass spectrometer having an ion source more directly open to the atmosphere should be more reliable and do show considerably higher values of O/O_2 [*Pokhunkov*, 1963*b*; *Schaefer and Nichols*, 1964]. The peak at mass 34, just barely detectable on a few spectrums, is attributed to the oxygen molecule containing an atom of O^{18}. The nitric oxide peak (30 amu) comes from charge exchange phenomena within the ion source of the mass spectrometer [*Potter*, 1955].

Carbon dioxide and water vapor, represented by 44 (CO_2^+) and 18 (H_2O^+) in Figure 5, have been consistently observed in the spectrums from the various rocket flights of the mass spectrometer and are presumed to come from the vehicle. There is also in the spectrums the secondary peak due to water vapor (OH^+ at 17 amu) with an amplitude of about 0.3 that of the 18-amu ion current peak, and a small peak at mass 12, probably due to C^+ from the carbon dioxide. The composition and origin of the small peak at mass number 26 (Figure 4) has not been explained.

Diffusive separation.   A summary of data on the distribution of argon and nitrogen is shown in Figure 8. All the data below 100 km were obtained from the laboratory analysis of gas samples collected by rocket-borne sample bottles flown at temperate latitudes. The first American samples were obtained from bottles flown on Aerobee rockets by Jones et al. of the Department of Aeronautical Engineering at the University of Michigan. The data shown in Figure 8 are from samples obtained from four Aerobee rockets and a V-2 rocket flown between 1950 and 1956 at White Sands Proving Ground in New Mexico. The samples, collected in steel bottles, were divided and analyzed by the group at the University of Michigan and by Professor Paneth of Mainz by separation of the various
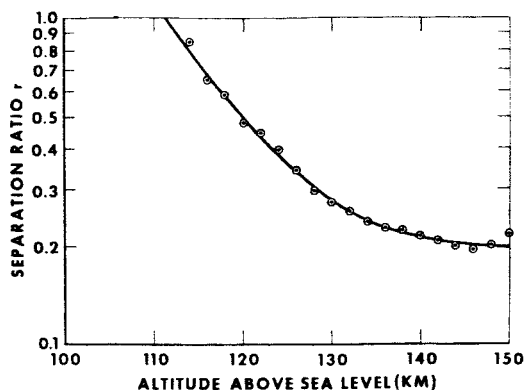
Fig. 7. The separation ratio r is the value of the ratio of the argon and molecular nitrogen densities measured in flight compared to the value for the same ratio measured for ground level air. This curve is for NASA 4.14, November 15, 1960, 1141 EST.

constituents. A comprehensive series of articles describing these experiments appears in the literature [*Jones et al.*, 1954; *Paneth*, 1954; *Reasbeck and Wiborg*, 1954; *Martin*, 1954]; a summary article of the program was written by *Wenzel et al.* [1960].

The University of Michigan work was continued with a quadrupole mass spectrometer on a Nike-Cajun rocket (NASA 10.91 UA) flown from Wallops Island, Virginia, at 1302 EST, May 18, 1962. The two dotted curves represent data from the upleg and downleg of the flight. The ion source was 'open,' immersed directly in the ambient atmosphere to minimize the probability of surface recombination of atomic oxygen [*Schaefer and Nichols*, 1964]. No satisfactory explanation has been found for the difference in profile between the two sets of measurements.

Scientists of the USSR collected a number of air samples on rocket flights from 1951 through 1956. Their techniques of collection and analysis were quite different from those employed in the United States. The containers were of glass, and the analyses were carried out by studying the emission lines of the gas when subjected to a high-frequency discharge. Their results, as presented in the summary article by *Mirtov* [1958], are also plotted in Figure 8.

Of the flights of the radio frequency mass spectrometer before the IGY program, only one, Aerobee NRL-13, yielded acceptable spectrums.

There was no evidence of diffusive separation of argon and molecular nitrogen in these data, at a maximum altitude of 137 km [*Townsend et al.*, 1954]. However, the nitrogen pressure in the spectrometer was about a factor of 10 greater than that which would be predicted from the various model atmospheres. We now believe that the data obtained constituted a better measure of the composition of the air escaping from the interior of the rocket's nose cone than of the ambient atmosphere.

The information about the distribution of argon and nitrogen obtained with radio frequency mass spectrometers flown by the USSR scientists has been summarized by *Pokhunkov* [1963a]. He found that both in the day and night atmospheres there is gravitational separation of argon and nitrogen. At night (midnight, September 23, 1960) this separation begins in the 105- to 110-km altitude region. The definition of this level in the day atmosphere was difficult: in the first two flights (morning, July 14 and 22, 1959) there were a limited number of data points near 100 km; in the last flight (late afternoon, November 15, 1961) the experiment began to record spectrums at 130 km. However, the data observed were in agreement for all three experiments and show appreciable separation of argon and nitrogen.

The data above 110 km shown in Figure 8 include the results from the mass spectrometers mounted on the pre-IGY rocket NN3.17 and the two IGY rockets NN3.18F and NN3.19F flown at Fort Churchill, Canada [*Meadows and Townsend*, 1960].

The pre-IGY flight occurred at 2321 CST on November 20, 1956. Although auroral activity was observed during the evening and ground magnetograms indicated a disturbed magnetic condition, an overcast sky prevented visual auroral observations at the time of firing. Though there may have been some auroral activity then, there was no evidence of a major display in progress. Care should be taken in extrapolating the curve of NN3.17 toward lower altitudes; since the temperatures in this region are low (200° to 250°K), it is expected that the separation ratio would attain a value of 1 somewhat above 100 km. The second firing, NN3.18F, was at 2002 CST on February 21, 1958. An auroral display observed visually was too weak and diffuse for ground camera record-
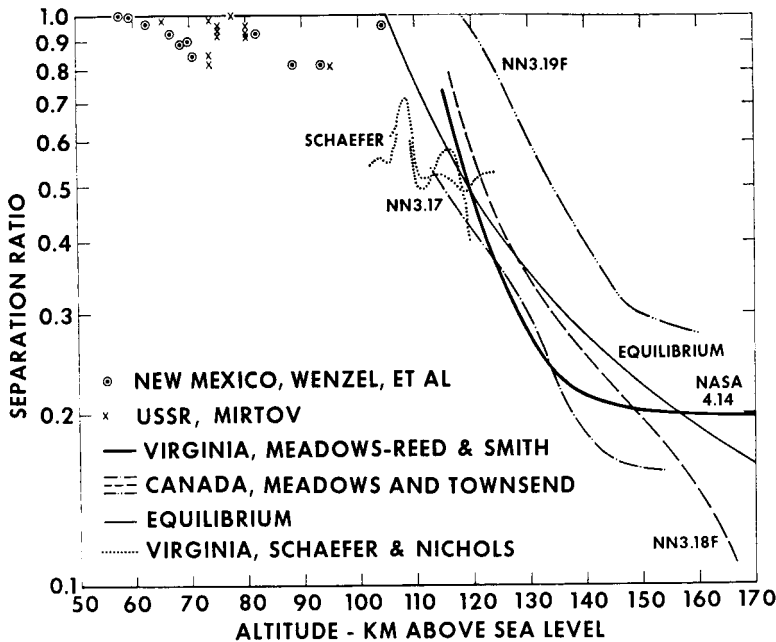
Fig. 8. Summary of data on the relative abundance of argon and nitrogen at various altitudes.
The USSR observations above 100 km are consistent with this pattern (see text).

ing; it is not known whether the vehicle entered the aurora.

It is believed that these two flights (NN3.17 and NN3.18F) can be considered typical of the arctic nighttime atmosphere.

The third rocket, NN3.19F, was flown at 1207 CST on March 23, 1958, during a polar blackout. An additional influx of energy, in the form of 10- to 100-Mev particles or X rays, or both, is associated with polar blackout. The absorption of this energy results in heating and turbulence, possibly changing both the extent of mixing and the temperature profile of the atmosphere.

The last flight, NASA 4.14, at 1141 EST, was made at a temperate latitude; ionograms indicated that the ionosphere was becoming quiet after a period of moderate disturbance. However, the Fredericksburg Magnetic Observatory at Corbin, Virginia, recorded a moderately severe magnetic storm from 0804 to 1221 EST, the sunspot number was high (133), and the solar flux at 10.7 cm was 183 $\times$ 10^{-22} w(m^2 c/s)$^{-1}$.

For comparison, a curve representing r under diffusive equilibrium conditions is shown. This was computed at 5-km intervals using the temperature curve of CIRA 1961 [*Kallmann-Bijl et al.*, 1961] up to 120 km; above 120 km the temperature profile was interpolated from the model atmospheres of *Harris and Priester* [1962] for the time and date of NASA 4.14. It was assumed that argon and molecular nitrogen behaved as ideal gases [*Meadows and Townsend*, 1958].

Conclusion. In conclusion, it can be said that the level at which diffusive separation of argon and molecular nitrogen becomes effective has been measured and found to vary from about 100 to 119 km, with typical values between 105 and 112 km.

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